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**Coordination Compounds of Aluminum as
Precursors to Aluminium Nitride**

By

Dr. Leonard V. Interrante

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Coordination compounds of aluminium as precursors to aluminium nitride*

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ABSTRACT

Two different systems have been examined as potential sources of aluminium nitride, an important electronic and structural ceramic material. Cyclic organoaluminium amides obtained as intermediates in the thermolysis of trialkylaluminium: ammonia Lewis acid-base complexes have been used to obtain AlN powder and as precursors for the chemical vapor deposition of AlN films. The structures of two of these intermediates were determined by single-crystal XRD and the kinetics and thermodynamics of their formation and thermal decomposition reactions were also studied.

The second system employs ethylenediamine as the Lewis base in combination with the R_3Al ($\text{R} = \text{Me}, \text{Et}$) compounds. A 2:1 ratio of Et_3Al with en yields a hydrocarbon-soluble, polymeric amide on thermolysis, which can be used to prepare AlN films by solution coating followed by pyrolysis in NH_3 . Lower proportions of R_3Al to en, on thermolysis, lead to the formation of $\text{R}_n\text{Al}(\text{en-2H})_m$ cluster species that contain 5- and 6-coordinated Al atoms chelated and bridged by en-2H ligands. On further heating, these cluster species apparently go on to form cross-linked, insoluble, polymeric networks through condensation reactions involving the multiple N-H and R-Al groups on the periphery of the cluster molecules. The structures of two of these novel Al-en cluster compounds were determined by single-crystal XRD.

* Dedicated to the memory of Professor John C. Bailar, Jr.

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1. INTRODUCTION

Aluminium nitride is a ceramic material whose properties make it attractive for a wide range of technological applications [1-7]. It is hard, it has a low density, a high thermal stability and is self-protecting in oxidizing environments. When pure, it conducts heat very well, yet its wide bandgap gives it high electrical resistivity and transparency throughout much of the IR and visible region. It is piezoelectric with a high acoustic wave velocity and its coefficient of thermal expansion matches that of silicon over a wide temperature range. Finally, it is a non-strategic material composed of terrestrially abundant elements.

On the other hand, its extreme hardness and high melting point make it difficult to prepare in the form of thin, adherent films, continuous fibers, or to sinter into dense, monolithic shapes; further, impurities seriously degrade its thermal and other desirable properties [2,6,7]. It is thus a difficult material to use in practice.

We are engaged in a continuing effort to design polymers and small molecules which can be directly converted to AlN in the purity and physical form required for use. One approach that we have employed is based on chemistry first reported by Wiberg (see ref. 8):



Unfortunately, the direct application of the procedure described by Wiberg gives AlN heavily contaminated with carbon. Moreover, this procedure, as described, is also unsuited for preparing thin films, continuous fibers or other "shaped" forms. On the other hand, the two starting materials in this reaction sequence, Me_3Al and NH_3 , have been employed in a chemical vapor deposition process to prepare AlN films, albeit at relatively high temperatures and with attendant problems in controlling composition, film morphology, etc. [9-11].

Over the past few years, we have carried out some detailed studies of the general reaction sequence represented in eqns. (1)-(4). Our objectives have been to understand this chemistry more fully and then apply what we have learned to obtain useful precursors to AlN. In these studies, we have employed other alkyl groups in place of methyl on the Al and isolated key intermediates for structural characterization. We have also carried out kinetic and thermodynamic measurements on the "parent" ($\text{R} = \text{Me}$) reaction sequence. In addition to providing specific information valuable in the design of suitable AlN precursor systems, these studies have contributed to the understanding of the factors that control the structure of organoaluminum amides. They have also provided an unusual opportunity to examine in detail

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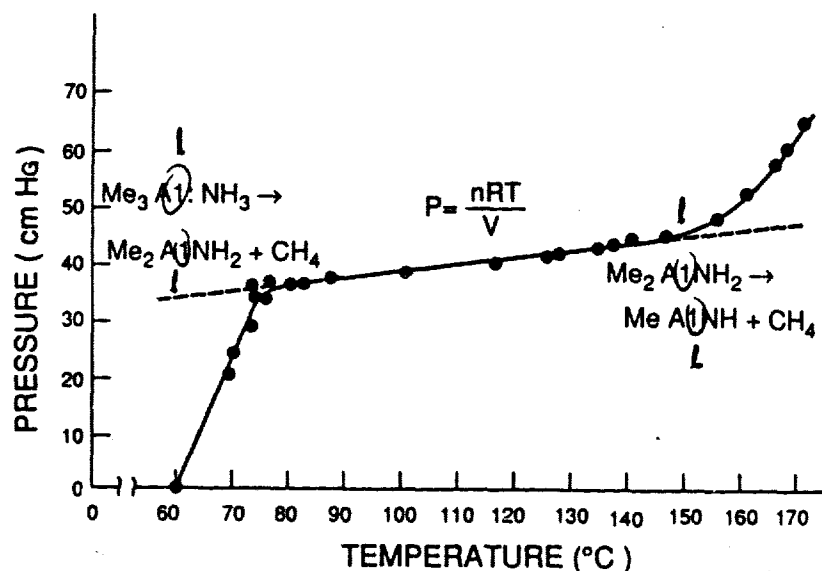
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the chemical transformations associated with the evolution of a molecular species into an important ceramic product.

2. STUDIES OF THE $\text{Me}_3\text{Al} + \text{NH}_3 \rightarrow \text{AlN} + 3\text{CH}_4$ REACTION SEQUENCE

Our initial studies of the reaction sequence shown in Scheme 1 involved the isolation of the initial 1:1 Lewis acid-base complex (or "adduct"), as well as the intermediate " Me_2AlNH_2 " amide, and the examination of the conversion of the adduct to the amide in a Pyrex glass pressure vessel [12]. The plot of system pressure vs. temperature in Fig. 1 was obtained by monitoring the pressure in the reactor while gradually increasing the reactor temperature. The onset of the sharp pressure increase vs. temperature was coincident with the melting of the adduct at ca. 55°C. By ca. 70°C, the liquid had solidified once again and the further pressure increase with temperature from there to ca. 140°C was found to correspond to that expected on the basis of the ideal gas equation. At 140°C, a second melting transition was observed and the pressure again increased more rapidly with increasing temperature. The gas evolved in this experiment was subsequently identified as methane by gas chromatography.

DSC studies of this process [13] yielded the enthalpy changes for the conversion of the neat adduct to amide and the amide to imide (reactions (2) and (3) in Scheme 1). No heat effect due to the final step in the conversion (reaction (4)) was found by DSC. In addition, the enthalpy change associated with the Lewis acid-base reaction,



letter "e" not
numeral "1".

Fig. 1. Changes in pressure accompanying the thermolysis of $(\text{CH}_3)_3\text{AlNH}_3$.

eqn. (1), was measured in benzene solution by adding $\text{NH}_3(\text{g})$ to a solution of Me_3Al . These enthalpy changes are given in Table 1.

The substantial ΔH for the first, NH_3 coordination, reaction is not surprising; similar values have been observed for related Lewis acid base reactions involving Me_3Al with organic amines [14]. The values for the next two reactions approximate well the difference between the strengths of the $\text{C-H} + \text{Al-N}$ bonds formed and the $\text{Al-C} + \text{N-H}$ bonds broken. This is consistent with the stepwise build-up of the tetrahedrally bonded AlN framework from the initial single Al-N bond/ Al-N unit in the $\text{Me}_3\text{Al}:\text{NH}_3$ adduct. The reason for the small ΔH in the last reaction is not clear; it may be an artifact due to the wide transition range.

These initial studies served to demonstrate the stepwise nature of at least the first two stages of the conversion of the adduct to AlN .

The intermediate organoaluminium amide, " Me_2AlNH_2 " is a crystalline solid that sublimes readily at ca. 70°C in vacuum and which is stable up to its melting point, ca. 140°C . On melting, it gradually converts to an insoluble, infusible solid of the approximate composition " MeAlNH ". Elemental analysis and solid-state NMR studies indicate that this is a material of variable composition with a complex, presumably crosslinked, polymeric structure involving four-coordinate Al atoms. This solid gradually loses methane on heating above 200°C to yield a black solid. Powder XRD studies of this solid do indicate the presence of AlN ; however, its black color and the results of elemental analyses suggest strongly that the final stage of the conversion is not as well defined as the two previous stages, and that at least some of the remaining Me groups are converted to elemental carbon.

1. STRUCTURES OF THE ISOLATED AMIDE INTERMEDIATES

As indicated above, the enthalpy data obtained for the first two stages of the thermal decomposition of the adduct are consistent with a stepwise conversion of the initial Lewis acid-base complex, which obviously has only one Al-N bond per AlN unit, to oligomeric and polymeric structures which have, respectively, two and three Al-N bonds per AlN unit. The oligomerization of the organoaluminium amides

TABLE 1
Enthalpies of reaction

Reaction	ΔH (kJ mol^{-1})
$\text{Me}_3\text{Al} + \text{NH}_3 \rightarrow \text{Me}_3\text{AlNH}_3$ (benzene solution)	-93
$\text{Me}_3\text{AlNH}_3 \rightarrow \frac{1}{3}(\text{Me}_2\text{AlNH}_2)_3 + \text{CH}_4$ (neat)	-82.2
$\frac{1}{3}(\text{Me}_2\text{AlNH}_2)_3 \rightarrow \frac{1}{n}(\text{MeAlNH})_n + \text{CH}_4$ (neat)	-71
$\frac{1}{n}(\text{MeAlNH})_n \rightarrow \text{AlN} + \text{CH}_4$ (neat)	0 (?)

and imides is well known [15], and can be considered as a natural consequence of the general tendency of Al to occur in a four-fold, pseudo-tetrahedral, coordination environment. While higher coordination numbers are known, they usually appear in compounds in which the steric requirements are somewhat unusual (vide infra).

In the case of the amides, $R_2AlNR'_2$, both dimeric and trimeric molecular species have been identified, with the NR'_2 groups serving as bridging ligands in a four- or six-membered $(AlN)_n$ ring system [15]. In the case of the R_2AlNH_2 amides, little detailed structural information was available prior to our investigation of this system, although Wiberg had suggested that the Me_2AlNH_2 compound was dimeric based on boiling point measurements in liquid ammonia. We were successful in obtaining single crystals of both this compound and its *t*-butyl analog, $(t-Bu)_2AlNH_2$, suitable for XRD studies [16].

Our structural studies of the Me_2AlNH_2 amide showed this molecule to be trimeric in the crystal with a skew-boat Al-N ring. The geometry about the Al and N is, as expected, pseudo-tetrahedral. However, the bond angles within the ring differ substantially from the ideal 109° . The N-Al-N bond angles average 101.4° ; the Al-N-Al 122.1° . This contrasts markedly with the behavior of the saturated hydrocarbon ring systems, where substantial deviations from tetrahedral geometry about carbon are uncommon. We hypothesize that these deviations are allowed principally by the large electronegativity difference between Al and N, and the resulting partial ionic character of the bonds. The hybridization requirements would be somewhat relaxed.

Unexpectedly, structural studies of the corresponding *t*-Bu derivative also indicated a trimeric ring structure (Fig. 2). The shape of this molecule is significantly different from that of the Me_2AlNH_2 amide, however. Whereas the $(AlN)_3$ ring in $(Me_2AlNH_2)_3$ is in the skew-boat conformation, in the *t*-butyl derivative it is planar, with a D_{3h} molecular symmetry. The Al and N atoms in this ring remain four-coordinated; however, the bond angles, particularly about Al, deviate substantially from the ideal tetrahedral values. The N-Al-N angle opens to 106.1° (compared with the 101.4° for the Me amide) and the Al-N-Al also opens, to an extraordinary 133.9° . The most plausible explanation for this unusual planar conformation is steric interference between the bulky *t*-butyl groups on neighboring Al atoms. In accord with this idea, the Al-N bond length increases from 1.958 \AA in $(Me_2AlNH_2)_3$ to 2.008 \AA in $(t-Bu_2AlNH_2)_3$. It is notable that the corresponding " $(Me_3Si)_2AlNH_2$ " compound, in which the *t*-Bu groups of the $(t-Bu_2AlNH_2)_3$ amide have been replaced by $SiMe_3$, is a dimer in the solid state, with a planar $(AlN)_2$ ring [17]. This may be due to the somewhat greater steric bulk of the $SiMe_3$ group relative to *t*-butyl, rendering the 1,3 or 1,2 interactions in the hypothetical trimeric form of the former compound energetically too costly.

In general, it seems likely that the ring size of these R_2AlNH_2 compounds represent a compromise between the opposing factors of ring strain and steric interactions among the 1,1-, the 1,2-, and the 1,3-substituents. A six-membered ring

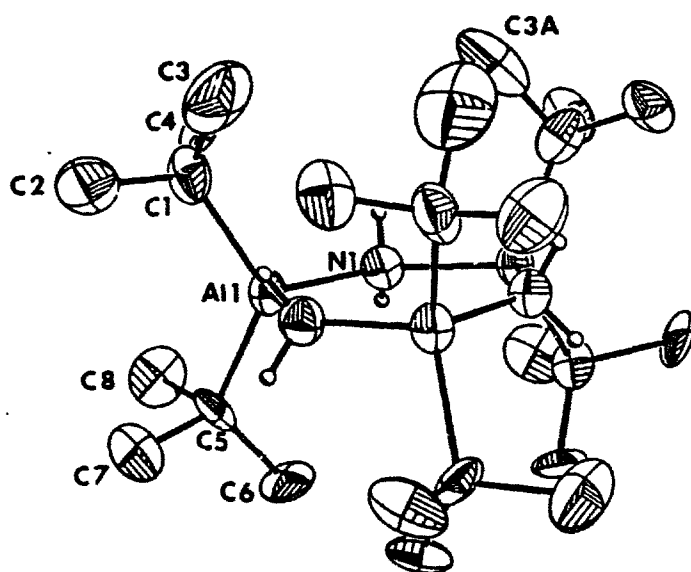


Fig. 2. Ortep plot of $(i\text{-Bu})_3\text{AlNH}_2$. Hydrogen atoms omitted (except on N) for clarity.

(trimer) in its chair conformation will have minimum ring strain but will have relatively large steric interactions between substituents. A four-membered ring (dimer) will have greater ring strain but less steric interference. Thus, larger substituents should favor dimer over trimer. The substituents in a smaller ring will also be more accessible to solvent; thus solvent-substituent combinations which strongly interact would favor the dimer. Entropy would be expected to favor the dimer, but preferential solvation of the dimer may reduce this effect.

In order to test this reasoning, we have examined the behavior of a series of related organoaluminium amides in aromatic solvents by NMR spectroscopy [18]. We found that each compound in the series $(\text{R}_3\text{AlNH}_2)_n$ (R = methyl, ethyl, *i*-butyl, *t*-butyl) participates in a dimer-trimer equilibrium in solution. Examination of our results given in Table 2 shows that, for R = Me, Et, and *i*-Bu, the larger the substituent, the more the equilibrium lies toward the dimer. ΔH becomes less positive as the substituent size increases; ΔS is positive for all substituents.

The *t*-butyl derivative has an anomalously high ΔH and a very high ΔS . We rationalize these results on the basis of differential solvation. Solvation will be principally due to the interaction of the aromatic π cloud of the solvent molecules with the highly positive N-H of these organoaluminium amides. For the first three compounds, the N-H groups are more accessible in the dimer than the trimer. Thus solvation will favor the dimer, making both ΔH and ΔS more negative than would be the case in the gas phase. Models show that the *t*-butyl groups are so large that

italic i

TABLE 2

Summary of thermodynamic results for the reaction $2(\text{trimer}) \rightleftharpoons 3(\text{dimer})$

Compound	ΔH (kJ)	ΔS (J K ⁻¹)	K_{eq}
(Me ₂ AlNH ₂) ₃	36 ± 0.7	12	5.5 × 10 ⁻³
(Et ₂ AlNH ₂) ₃	20 ± 2	15	2.8 × 10 ⁻³
(i-Bu ₂ AlNH ₂) ₃	14 ± 2	30	4.3 × 10 ⁻¹
(t-Bu ₂ AlNH ₂) ₃	30 ± 1	104	17
(Me ₂ AlN(CH ₃) ₂) ₃	69 ± 7	72	1.3 × 10 ⁻⁶

→ Hol
→ g/±

the N-H protons are probably not solvated in either the dimeric or trimeric forms. The results for this compound are thus a better representation of the intrinsic behavior of the molecule, undistorted by solvent effects.

Also given in Table 2 are data for a related compound, [Me₂AlN(CH₃)₂]₃, in which the substituent group on the N is part of a three-membered ethyleneimine ring. In going from trimer to dimer, the bond angles within the (Al-N)_n ring must tend to decrease, causing an increase in the exocyclic bond angle at the nitrogen. When the nitrogen substituents are small hydrogen atoms, this is of little consequence. However, when the nitrogen substituents are bound into an already strained three-membered ring, any tendency toward expansion of the bond angle within this ring will be very strongly resisted. Solvation of this molecule should be weak in comparison with the N-H compounds. The very large ΔH and ΔS confirm this analysis.

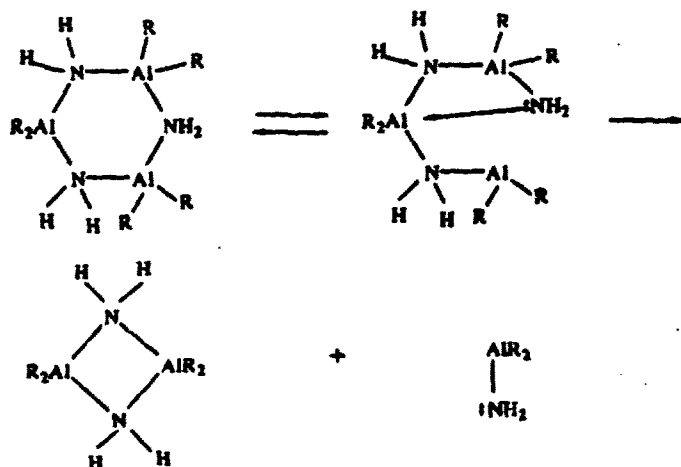
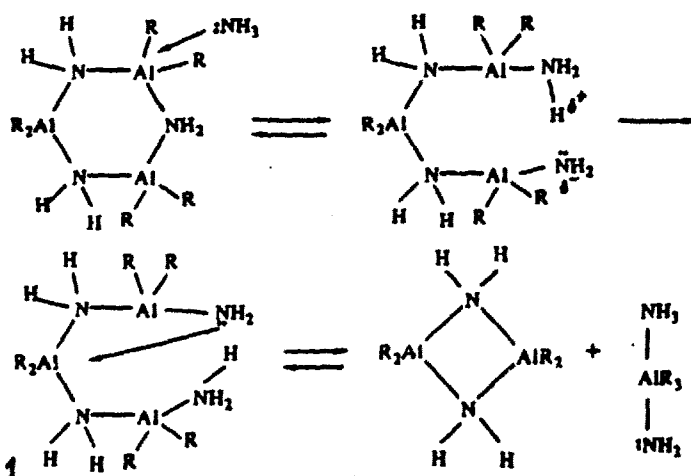
The monomeric form Me₂AlNH₂ has been implicated as an intermediate in the decomposition of the Lewis acid-base adduct in solution [13] and has also been suggested to exist in the vapor phase during MOCVD of AlN using the trimeric amide [19,20]. We therefore performed generalized valence bond calculations (GVB) on this species and the related H₂AlNH₂ and H₂SiCH₃ to determine the equilibrium structures [21]. Each is predicted to have a planar molecular structure with Al=N (or Si=C) double bonds and overall C_{2v} symmetry. The Al=N bond lengths are predicted to be 1.80 and 1.78 Å, respectively, significantly less than the 1.958 Å observed in the methyl trimer. Taken along with the planarity, this implies a significant amount of double bond character. The optimized Si=C bond length is somewhat less, 1.74 Å. Viewing the Al=N bond as one covalent plus one dative bond, and the Si=C as two covalent bonds, the longer Al=N distance is a reasonable consequence of the generally greater length of dative bonds.

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We are currently attempting to prepare the monomeric Me₂AlNH₂ species in the gas phase by vapor-phase pyrolysis of the adduct, and to measure its microwave spectrum. If successful, this experiment should allow the determination of the actual bond angles and distances for this species and thereby a direct comparison with the predictions of this theoretical study.

4. MECHANISMS

During the dimer-trimer equilibrium study, we noted that the rate of equilibration decreased rapidly with increasing Al substituent size [18]. Of particular note, amine exchange was rapid, and NH_3 strongly catalyzed the equilibration. The mechanism in Schemes 2(a) and 2(b) was advanced to explain these observations.

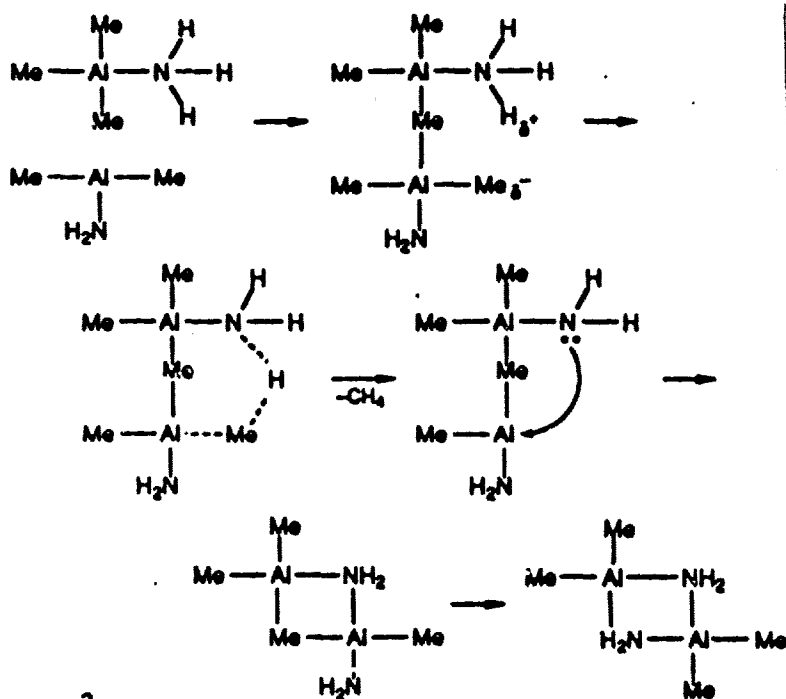
Uncatalyzed NH_3 -Catalyzed

Scheme 2 Proposed mechanism for the $[\text{R}_2\text{AlNR}_2]_3$ trimer-dimer interconversion. (a) Uncatalyzed; (b) catalyzed.

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The ability of NH_3 to open (AlN) rings suggests an explanation for our empirical observations [12] that pyrolysis of the R_2AlNH_2 ($\text{R} = \text{Me}, \text{Et}$) amides under ammonia yields AlN of improved purity and crystallinity. The initial stages of AlN formation by $(\text{R}_2\text{AlNH}_2)_3$ pyrolysis are suspected to proceed by linkage of the rings into a network. It is probable that during this process, some Al-R groups are left without H atoms on neighboring nitrogens. In addition, regions may form in which the rings are misaligned, such that an aluminium atom on one ring is adjacent to an aluminium of the next ring, rather than a nitrogen. Fusion of such rings is not possible. Ammonia, by allowing ring opening, would facilitate skeletal rearrangement under mild conditions so that RH elimination may occur instead of pyrolysis of the R groups. It may also serve as an alternative source of hydrogen in the final conversion of (RAINH) to AlN, thereby circumventing the pyrolysis of isolated Al-R groups to carbon and hydrogen. Improved purity and crystallinity would naturally follow.

The mechanism of Me_3AlNH_2 decomposition in solution was also studied [13]. The reaction was found to be autocatalytic, with monomeric Me_2AlNH_2 , as the Lewis acid catalyst (Scheme 2), forming the methyl-bridged intermediate ($\mu\text{-Me}$)



Scheme 2. Proposed mechanism for the thermal decomposition of Me_3AlNH_2 .

$(\text{Me}_2\text{AlNH}_2)(\text{Me}_2\text{AlNH}_3)$. This then loses methane by proton transfer and rearranges to the dimeric form of the product. The reaction is inhibited by NH_3 and catalyzed by the monomeric Me_3Al . The unstable $(\mu\text{-NH}_2)(\mu\text{-Me})\text{Al}_2\text{Me}_4$ appears as an intermediate in the Me_3Al -catalyzed reaction.

3. CVD STUDIES EMPLOYING $[\text{Me}_2\text{AlNH}_2]_3$

Although Me_3Al and NH_3 have been widely employed as separate source precursors in the CVD of AlN films, the tendency to form an adduct on mixing of these species in the gas phase, coupled with the relatively low volatility of that adduct, have rendered the use of this mixed precursor system problematic [9-11]. Also, the control of product stoichiometry requires the use of a large excess of NH_3 , as CVD using Me_3Al alone produces carbon-containing Al films. Finally, the temperatures that have been reported for the successful application of this precursor system are in excess of 1000°C , which is substantially higher than that which can be tolerated for many potential applications for AlN films.

On the basis of the significant volatility observed for $[\text{Me}_2\text{AlNH}_2]_3$, as well as its structural and compositional relationship to AlN (Fig. 3), we reasoned that these problems associated with the separate Al and N sources might be overcome through the use of $[\text{Me}_2\text{AlNH}_2]_3$ as a single-source precursor to AlN. Our initial efforts employing a simple low-pressure, hot-wall CVD system and $[\text{Me}_2\text{AlNH}_2]_3$ alone gave high-quality, polycrystalline AlN films at temperatures of ca. 500°C or greater, appreciably lower than that previously employed for the $\text{Me}_3\text{Al} + \text{NH}_3$ system [22].

Recently, we have been investigating the gas-phase species produced in such a hot-wall CVD system employing $[\text{Me}_2\text{AlNH}_2]_3$ by means of molecular beam mass spectrometry [19,20]. Our preliminary results suggest the existence of not only the dimeric and trimeric form of the amide in the gas phase, but also the formation of higher molecular weight oligomers which appear to result from the gas-phase condensation reaction of these trimer and dimer species. We are continuing these studies of

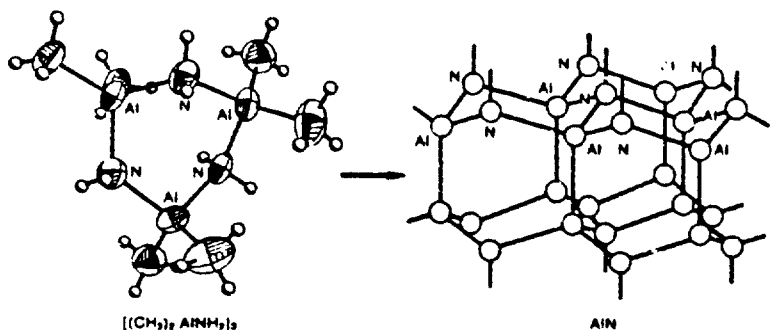


Fig. 3. Structural relationship between $[\text{Me}_2\text{AlNH}_2]_3$ and AlN.

the gas/surface chemistry associated with the deposition of AlN using $[\text{Me}_2\text{AlNH}_2]_3$ in order to compare the processes occurring under CVD conditions with those in condensed phases.

6. STUDIES OF THE $\text{R}_3\text{Al}:\text{en}$ SYSTEM

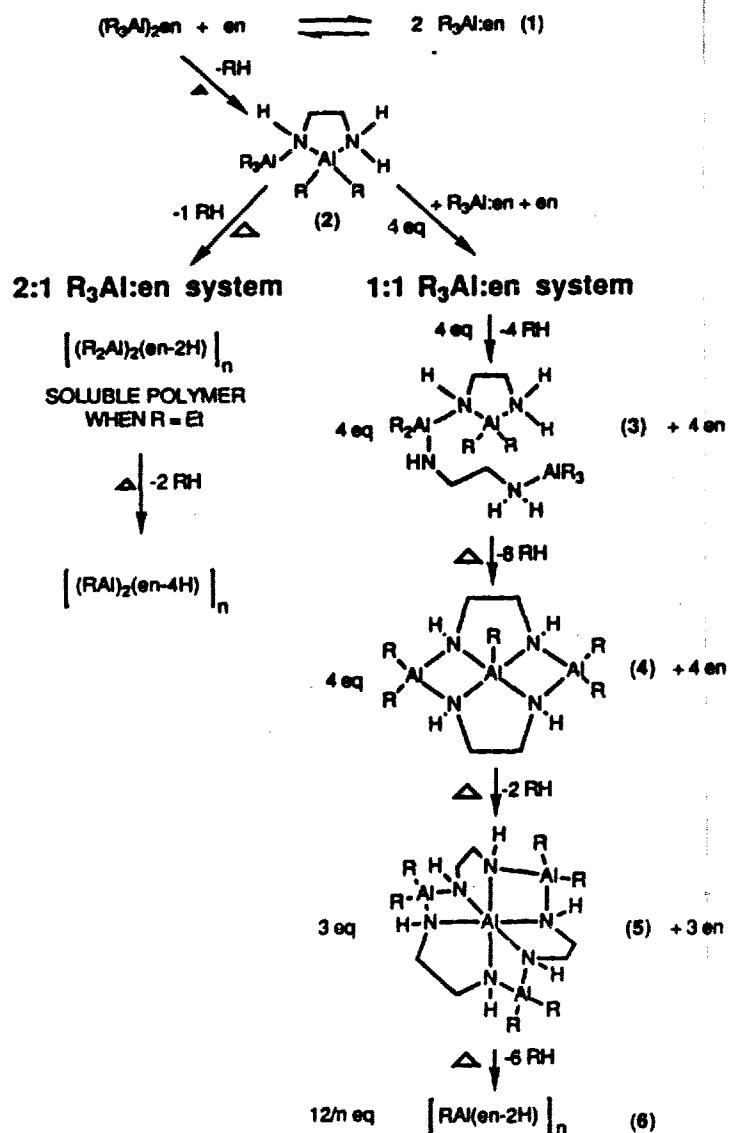
The cyclic oligomer obtained from the reaction sequence described by Wiberg (Scheme 4) has served as a useful CVD precursor to AlN. The corresponding diethylaluminium amide was pyrolyzed in NH_3 to high purity, high surface area AlN powder [12]. For many purposes, however, a processable polymer is more desirable. In pursuit of such polymeric systems, we undertook the investigation of the reactions of the R_3Al ($\text{R} = \text{Me}$ and Et) with a difunctional amine, ethylenediamine (en) [23-25].

These reactions were conducted using two different ratios of the trialkylaluminium compounds with en. A 2:1 mixture of Et_3Al and ethylenediamine heated for 12 h at 80°C was found to yield a viscous, hydrocarbon-soluble polymer with a molecular weight near 1600. On the other hand, a 1:1 ratio of these two components gave an intractable solid under the same reaction conditions. The composition of both polymers corresponded approximately to that expected for the loss of one mole of ethane per Et_3Al , forming diamides or monoamides from the diamine.

In an effort to determine the origin of the differences observed for the properties of these two amides, and to investigate the pathways by which these amides are formed, we undertook a detailed study of these reactions with the aid of solution NMR (^1H , ^{13}C , and ^{27}Al) and IR spectroscopies, as well as by carrying out GC, TGA, DSC and elemental analyses on the intermediate and final products. In the case of the $\text{R} = \text{Me}$ compounds, we were also able to isolate two key intermediates along the way to the final polymeric amides and to obtain single crystals suitable for XRD.

Our results suggest that the thermolyses of the two $\text{R}_3\text{Al}:\text{en}$ adducts in hydrocarbon solutions proceed through a common chelated $\text{Al}(\text{en}-\text{H})$ derivative, $[(\text{R}_3\text{Al}(\text{en}-\text{H})(\text{R}_2\text{Al}))_2]$ (2). As is illustrated in Scheme 2, the fate of this intermediate depends on the availability of uncomplexed en and/or the 1:1 $\text{R}_3\text{Al}:\text{en}$ adduct, which can react with the intermediate 2, so as to produce $\text{R}_{3x-2n}\text{Al}_x(\text{en}-2\text{H})_n$ cluster species that contain five- and six-coordinated Al atoms. These cluster species then apparently go on to form cross-linked, insoluble, polymeric networks through condensation reactions involving the multiple N-H and Me-Al groups on the periphery of the cluster. In the case of the 2:1 $\text{R}_3\text{Al}:\text{en}$ mixture, we postulate that the lack of appreciable en or 1:1 $\text{R}_3\text{Al}:\text{en}$ adduct in solution leads to self-condensation of the initial intermediate 2, through the R_2Al and NH_2 groups available on each monomer unit, to form a linear, soluble (for $\text{R} = \text{Et}$), polymeric amide of the approximate composition $[\text{RAl}(\text{en}-2\text{H})]_n$.

In the case of the $\text{Me}_3\text{Al}:\text{en}$ mixtures involving a higher Al:en ratio, we were able to isolate two distinct intermediates and to determine their molecular structures

Comparison of the 2:1 and 1:1 $R_3Al:en$ SystemsScheme 1. Suggested pathways for the thermal decomposition of the $(R_3Al)_n$ adducts.

3

move up

by single crystal XRD. The novel structures of these two intermediates, in which en-2H ligands both chelate and bridge Al atoms to form $\text{Me}_2\text{Al}(\text{en-2H})_n$ clusters, are shown in Figs. 4 and 5. The $\text{MeAl}[(\text{HNCH}_2\text{CH}_2\text{NH})\text{AlMe}_2]_2$ cluster, which is illustrated in Fig. 4, contains one central five-coordinated Al atom in a distorted trigonal bipyramidal environment connected to two four-coordinated, pseudo-tetrahedral Al atoms by $-\text{NH}$ bridges [25]. In the presence of additional en, this

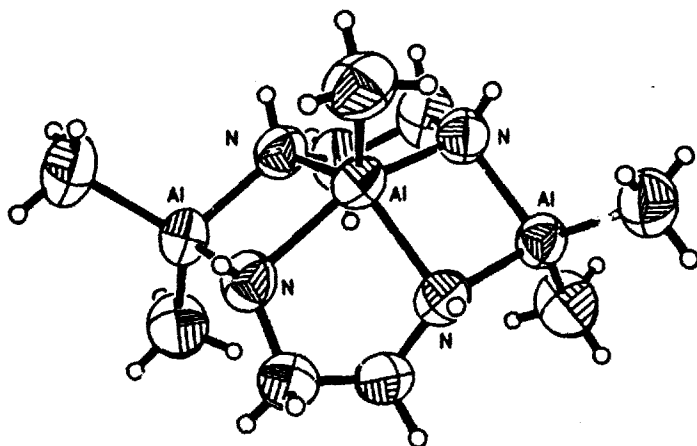


Fig. 4. Ortep plot of the $\text{MeAl}[(\text{HNCH}_2\text{CH}_2\text{NH})\text{AlMe}_2]_2$ structure.

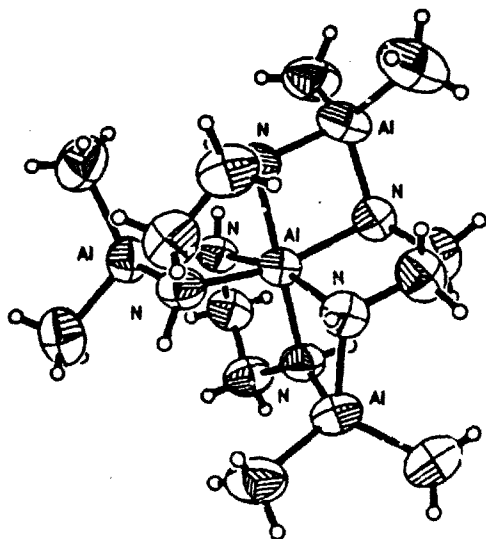


Fig. 5. Ortep plot of the molecular structure of $\text{Al}[(\text{HNCH}_2\text{CH}_2\text{NH})\text{AlMe}_2]_3$.

species goes on to form a higher nuclearity cluster, $\text{Al}[(\text{HNCH}_2\text{CH}_2\text{NH})\text{AlMe}_2]_3$ [23], that contains a rare six-coordinated, AlN_6 species in a distorted octahedral configuration surrounded by three other four-coordinated Al atoms (Fig. 5). These three R_2Al species bridge the en-2H ligands of the central pseudo-octahedral $\text{Al}(\text{en-2H})_3$ complex to form three, four-membered, Al_2N_2 rings.

7. CONCLUSION

In summary, our on-going studies of organoaluminium amides as precursors to AlN have already yielded some novel structures and reactions, as well as some potentially useful routes to AlN powder and films. At the same time, these studies have provided new information regarding the factors that control the structures and reactivity of this class of aluminium coordination compounds.

Our current efforts are directed primarily to the detailed study of the chemistry occurring during CVD of AlN using $[\text{Me}_2\text{AlNH}_2]_n$. Molecular beam sampling of the gaseous species present in a hot-wall CVD reactor are being combined with microwave studies of the adduct and amide in the gas phase. We are also examining the surface chemistry by temperature programmed desorption and other methods. Our aim in these studies is to understand the gas-phase and surface chemistry of this system in sufficient detail to allow its effective use in the MOCVD of AlN. We are also examining the possibility of preparing AlN/TiN solid solutions or nanocomposites using aluminium and titanium amides as precursors.

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